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(54) **Additive concentrates for distillate fuels.**

(57) An additive concentrate for incorporation into wax containing petroleum fuel oil compositions to improve low temperature flow properties comprising an oil solution containing:

- (A) a C₃₀-C₃₀₀ oil-soluble nitrogen salt and/or amide compound was crystal growth inhibitor formed by reaction of alicyclic C₄ to C₁₀ carboxylic acid and long chain secondary amine;
- (B) an organic acid to improve the solubility of (A) in the oil, which acid includes non-linear carboxylic acids including branched or unsaturated fatty acids, aromatic acids, e.g. benzoic acid, phenols, and organic phosphorus containing acids; and
- (C) a copolymer of ethylene and an unsaturated ester, e.g. vinyl acetate.

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'ADDITIVE CONCENTRATES FOR DISTILLATE FUELS'

1. Field of the Invention

This invention relates to additives to improve the flow and filterability properties of distillate fuels at low temperatures, to fuels containing the additives and especially to concentrates of the additives for incorporation into the fuel. Particularly, the invention relates to an additive concentrate comprising an oil solvent, an ethylene-ester copolymer, a nitrogen-containing amide and/or salt of an aliphatic dicarboxylic acid or anhydride, and an oil soluble compatibility improving additive which lowers the pour point of said concentrate and which improves the compatibility of said copolymer and said nitrogen compound.

2. Description of the Prior Art

Additive systems and concentrates comprising nitrogen containing amide or amine salts as used in the present invention are disclosed in U.S. Patent 4,211,534 which discloses an additive flow improver of an ethylene polymer or copolymer, a second polymer of an oil soluble ester and/or C₃ and higher olefin polymer and a nitrogen containing compound.

European Patent publication 0061894 discloses the use of nitrogen containing compounds in combination with certain ethylene/vinyl acetate copolymers as distillate additives which may be supplied in the form of concentrates.

U.S. Patent 3,982,909 discloses an additive system comprising amides, diamides and ammonium salts alone, or in combination with certain hydrocarbons such as microcrystalline waxes or petrolatums, and/or an ethylene backbone polymeric pour depressant, the combination being useful as a flow improver for middle distillate fuels.

1 U.S. Patent 3,850,587 shows use of certain
2 acids, especially aromatic acids, to improve the compati-
3 bility of the amine salt/amides of alkenyl succinic acid
4 and ethylene-vinyl acetate copolymers in oil concentrates
5 used for incorporation into distillate fuels.

6 BRIEF SUMMARY OF THE INVENTION

7 While nitrogen containing derivatives of ali-
8 phatic polycarboxylic acids are effective in inhibiting wax
9 crystal growth and as cold flow improving additives, along
10 with ethylene-unsaturated ester copolymers, they usually
11 have low solubilities and tend to crystallize out of oil
12 concentrates at ambient temperatures rendering the con-
13 centrate difficult to use. Also, they tend to interact
14 with the copolymer of ethylene and unsaturated ester, e.g.
15 copolymer of ethylene and vinyl acetate, to thicken the oil
16 concentrate. In fact, they can gel the concentrate to a
17 solid in some cases. This interaction can require exces-
18 sive amounts of solvent or diluent oil in order to keep the
19 concentrate fluid so it can be easily poured and handled.
20 The present invention is based on the discovery that the
21 fluidity and pour point of an additive concentrate con-
22 taining a copolymer of ethylene and unsaturated ester, with
23 an amine salt, e.g. an alkyl ammonium, or amide compound,
24 having a total of 30-200, preferably 50-150 carbon atoms,
25 derived from certain aliphatic carboxylic acids or anhy-
26 drides, optionally in combination with still other addi-
27 tives, may be improved by the incorporation of certain
28 compatibility improving agents.

29 Composition Of The Invention

30 Concentrates may be prepared comprising: (A)
31 one part by weight of the oil-soluble nitrogen compound
32 which may be amides and/or amine salts of acyclic aliphatic
33 carboxylic acids or ammonium salts of said acids or anhy-
34 drides thereof; (B) 0.005 to 1.0, e.g. 0.01 to 0.4, pre-

1 ferably 0.02 to 0.10 parts by weight of an oil-soluble
2 acidic compound which acts as a compatibility improver
3 agent; and (C) about 0.01 to 10, e.g. 0.03 to 5, preferably
4 0.05 to 5 parts by weight of oil-soluble ethylene-unsatu-
5 rated ester distillate flow improver copolymer. Concen-
6 trates in a mineral oil as a solvent and/or diluent, such
7 as naphtha, of 30 to 80, preferably 40 to 70 wt. % of the
8 additive combination (A), (B) and (C) will generally be
9 used. Aromatic solvents or aromatic containing oils, such
10 as heavy aromatic naphtha (HAN) are particularly suitable
11 for dissolving the aforesaid components to make concen-
12 trates.

13 The concentrates may also contain still other
14 additives, in the additive mixture besides (A), (B) and (C)
15 such as 0.01 to 10 parts by weight of each other additive,
16 per part by weight of said nitrogen compound. Examples of
17 other additives include other polymers including polyesters
18 such as polyacrylates or polymethacrylates, and the other
19 polymers described in col. 6, line 57 to col. 10, line 6 of
20 U.S. 4,210,424; waxes such as normal paraffin waxes, slack
21 waxes, foots oil and other waxes as described in col. 4,
22 line 39 to col. 5, line 16 and col. 11, line 45 to col. 12,
23 line 6 of U.S. 4,210,424; hydrocarbon polymers including
24 ethylene-propylene copolymers, polyisobutylene as well as
25 other hydrocarbon polymers as described in col. 4, line 61
26 to col. 6, line 68; as well as other conventional additives
27 found useful in treating fuel oil.

28 The flow improver concentrates of the present
29 invention may be incorporated into a broad category of
30 petroleum fuel oils, especially distillate fuels boiling in
31 the range of about 120°C to about 500°C (ASTM D1160),

1 preferably those distillate fuels boiling in the range of
2 about 150°C-400°C to improve their flow properties. The
3 most common petroleum distillate fuels are kerosene, jet
4 fuels, diesel fuels and heating oils. Low temperature flow
5 properties are most usually encountered with diesel fuels
6 and with heating oils.

7 The concentrates will generally be included in
8 the fuel to give a total additive concentration of (A), (B)
9 and (C) in the fuel of about 0.001 to 0.5 wt. %. Excellent
10 results are usually achieved with said total additive con-
11 centrations in range of 0.005 to 0.25 wt. %, preferably in
12 the range of about 0.005 to 0.05 wt. %. All said weight
13 percents being based upon the weight of distillate fuel.

14 The Nitrogen Compound

15 The nitrogen-containing wax crystal growth in-
16 hibitors used in the compositions of the invention are
17 generally those having a total of 30-300, preferably 50-150
18 carbon atoms, and being oil-soluble amine salts and/or
19 amides formed by reacting at least 1, generally at least 2,
20 molar portions of a hydrocarbyl substituted amine per molar
21 portion of the aliphatic acyclic polycarboxylic acid, e.g.
22 2 to 4 carboxyl groups preferably dicarboxylic acids, or
23 their anhydrides. All acid groups may be converted to
24 amine salts or amides, or part of the acid groups may be
25 converted to esters by reaction with hydrocarbyl alcohols,
26 or part of the acid groups may be left unreacted.

27 Examples of aliphatic, acyclic carboxylic acids
28 used to prepare these materials include C₄ to C₁₀, e.g. C₄,
29 saturated, but preferably unsaturated, aliphatic hydro-
30 carbyl carboxylic acids, such as: maleic, fumaric, suc-
31 cinic, succinic anhydride, adipic, glutaric, sebacic, ma-
32 lonic, citric, derivatives and mixtures of the foregoing,
33 etc.

1 Preferred amines used to prepare the amine
2 salts and/or amides include alkyl amines having alkyl
3 groups of C₈ to C₃₀ carbon atoms, preferably 10 to 24
4 carbon atoms, preferably secondary amines.

5 Amine mixtures may also be used and many amines
6 derived from natural materials are mixtures. Thus, coco
7 amine derived from coconut oil is a mixture of primary
8 amines with straight chain alkyl groups ranging from C₈ to
9 C₁₈. Another example is tallow amine, derived from
10 hydrogenated tallow, which amine is a mixture of C₁₄ to
11 C₁₈ straight chain alkyl groups.

12 To prepare the ester derivatives, preferably C₈
13 to C₃₀, e.g. C₁₀ to C₂₄, saturated or unsaturated
14 aliphatic, hydrocarbyl alcohols can be used, including
15 cracked wax Oxo-alcohols, and aldol derived alcohols. Spe-
16 cific examples of these alcohols include 1-tetradecanol,
17 1-hexadecanol, 1-octadecanol, C₁₂ to C₁₈ Oxo alcohols made
18 from a mixture of cracked wax olefins, 1-hexadecanol and
19 1-octadecanol, etc.

20 The amides can be formed in a conventional man-
21 ner by heating the amine and acid with the removal of any
22 water generated by the action. Similarly the monoester is
23 prepared in a conventional manner by heating the alcohol
24 and the acid to effect the reaction and promote removal of
25 the water of reaction if generated from the reaction en-
26 vironment. The salts are also conventionally prepared by
27 simply mixing secondary amine and the acid, or acid anhy-
28 dride, or monoester or monoamide of the acid, together with
29 stirring at room temperature, e.g. 25°C.

30 Particularly preferred are nitrogen compounds of
31 the above type that are prepared from dicarboxylic acids,
32 which appear to be generally more effective than compounds
33 prepared from monocarboxylic acids or tricarboxylic acids.

1 It is preferred that the nitrogen containing
2 compound has at least one straight chain alkyl segment
3 extending from the compound containing 8-30, preferably
4 10-24 carbon atoms. Preferably the nitrogen compound con-
5 tains at least three alkyl chains each containing from 8 to
6 30 carbon atoms and preferably at least two of these chains
7 are normal. Also at least one ammonium salt, amine salt or
8 amide linkage is required to be present in the molecule.
9 The particularly preferred compound is the amide-amine salt
10 formed by reacting 1 molar portion of maleic anhydride with
11 2 molar portions of di-hydrogenated tallow amine. Another
12 preferred embodiment is the diamide formed by dehydrating
13 this amide-amine salt.

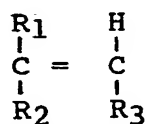
14 The Compatibility Improver

15 The acids for use in the concentrates of the
16 present invention are oil-soluble organic acids, including
17 their anhydrides, containing 3 to 100, e.g. 6 to 30, pre-
18 ferably 6 to 24 carbons and having 1 to 3, preferably 1 to
19 2 acid groups. While their method of operation is not
20 fully understood, it is believed that they may inhibit the
21 interaction of the basic nitrogen compound with the ethy-
22 lene-unsaturated ester copolymer to hinder gelling or undue
23 viscosity increase of the oil. Examples of suitable acids
24 include non-linear carboxylic acids which may be aromatic,
25 aliphatic, branched, or unbranched, saturated or unsatu-
26 rated, substituted or unsubstituted, provided that the acid
27 is non-linear e.g. that it is not straight chain, saturated
28 and non-substituted. Aromatic carboxylic acids appear
29 especially useful as are phenols, and phosphorus acids.
30 Preferred are weak acids such as fatty acids, benzoic acid,
31 phenol, alkyl phenols, dicarboxylic acids such as maleic
32 anhydride, alkenyl or alkyl succinic acid or anhydride,
33 organic phosphates such as dialkyl, mono acid phosphate,
34 etc.

The Ethylene Copolymer

The ethylene copolymers are of the type known in the art as wax crystal modifiers, e.g. pour depressants and cold flow improvers for distillate fuel oils. Usually, they will comprise about 3 to 40, preferably 4 to 20, molar proportions of ethylene per molar proportion of ethylenically unsaturated ester monomer, which latter monomer can be a single monomer or a mixture of such monomers in any proportion. These polymers will generally have a number average molecular weight in the range of about 500 to 50,000, preferably about 1000 to 20,000, e.g. 1000 to 6000, as measured for example by Vapor Pressure Osmometry (VPO), such as using a Mechrolab Vapor Pressure Osmometer Model 302B.

The unsaturated monomers, copolymerizable with ethylene, include unsaturated mono and diesters of the general formula:



wherein R_1 is hydrogen or methyl; R_2 is a $-OOCR_4$ or $-COOR_4$ group wherein R_4 is hydrogen or a C_1 to C_{28} , more usually C_1 to C_{16} , and preferably a C_1 to C_8 , straight or branched chain alkyl group; and R_3 is hydrogen or $-COOR_4$. The monomer, when R_1 and R_3 are hydrogen and R_2 is $-OOCR_4$, includes vinyl alcohol esters of C_1 to C_{29} , more usually C_1 to C_{17} , monocarboxylic acid, and preferably C_2 to C_5 monocarboxylic acid. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, vinyl palmitate, etc. When R_2 is $-COOR_4$ and R_3 is

1 hydrogen, such esters include methyl acrylate, isobutyl
2 acrylate, methyl methacrylate, lauryl acrylate, C₁₃ Oxo
3 alcohol esters of methacrylic acid, etc. Examples of mono-
4 mers where R₁ is hydrogen and either or both of R₂ and R₃
5 are -COOR₄ groups, include mono and diesters of unsaturated
6 dicarboxylic acids such as: mono C₁₃ Oxo fumarate, di-C₁₃
7 Oxo fumarate, di-isopropyl maleate, di-lauryl fumarate,
8 ethyl methyl fumarate, etc. It is preferred, however, that
9 the acid groups be completely esterified as free acid
10 groups tend to promote haze if moisture is present in the
11 oil.

12 Copolymers of ethylene and unsaturated esters,
13 and methods for their manufacture, are well known in the
14 art of distillate flow improvers and have been described in
15 numerous patents such as U.S. 4,211,534; 3,961,916; and
16 4,087,255. Copolymers of ethylene and vinyl acetate are
17 particularly preferred.

18 Oil-soluble, as used herein, means that the
19 additives are soluble in the fuel at ambient temperatures,
20 e.g., at least to the extent of about 0.01 wt. % additive
21 in the fuel oil at 25°C., although at least some of the
22 additive comes out of solution near the cloud point in
23 order to modify the wax crystals that form.

24 The invention will be further understood by
25 reference to the following Example which includes preferred
26 embodiments of the invention.

27 Example 1, Part A

28 In carrying out this Example, the following
29 additive materials were used:

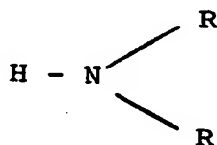
1 Polymer 1

2 Polymer 1 used in this Example an ethylene-vinyl
3 acetate copolymer of about 62 wt. % ethylene and about 38
4 wt. % vinyl acetate, which had a number average molecular
5 weight of about 1800 (VPO). It is identified in said U.S.
6 Pat. No. 3,961,916 as Copolymer B of Example I (column 8,
7 lines 25-35).

8 Nitrogen Compound A

9 Nitrogen Compound A was a diamide of maleic
10 anhydride and secondary hydrogenated amine formed by re-
11 acting one mole of maleic anhydride with two moles of Ar-
12 meen 2HT with heating in a solvent to a temperature suf-
13 ficient to remove all the water and thereby form the di-
14 amide in accordance with U.S. Patent 3,982,909.

15 The secondary hydrogenated tallow amine, derived
16 from tallow fat is a commercially available product sold by
17 Armak Co., Chemicals Division, Chicago, Ill. and designated
18 Armeen 2HT. This amine has the formula:



19 where the R's are straight chain alkyl groups derived from
20 hydrogenated tallow and are about 4% C₁₄ alkyl groups, 31%
21 C₁₆ alkyl groups and 59% C₁₈ alkyl groups.

25 Heavy Aromatic Naphtha (HAN)

26 This is a useful solvent for the multicomponent
27 additives of the invention and typically has an aniline
28 point of 24.6°C., a specific gravity (°API) of 0.933, a
29 boiling range of 179°C. to 235°C. and is composed of 4 wt.
30 % paraffins, 6.7 wt. % naphthenes, 87.3 wt. % aromatics,
31 e.g. polyalkyl aromatics, and 2.0 wt. % olefins.

Concentrates A, B and C

Concentrates A, B, and C were prepared consisting of the active ingredient (a.i.) Polymer 1 and Nitrogen Compound A, dissolved in HAN, wherein one part by weight of Compound A was used per part by weight of Polymer 1. The amount of HAN was adjusted to give 53 wt. % HAN (Concentrate A); 51% (Concentrate B) and 67% (Concentrate C). These concentrates were then tested for pour point (ASTM D-97) and the results are summarized in Table I.

Table IEffect of Additive Concentration on Pour Point

<u>Concentrate</u>	<u>WT.% a.i.</u>	<u>Wt.% HAN</u>	<u>Appearance</u>	<u>ASTM Pour, °F</u>
A	47	53	Solid	90
B	49	51	Solid	85
C	33	67	Liquid	60

As seen by Table I, 33% active ingredient content of the concentrate gave a liquid concentrate at room temperature with a pour point of 60°F. However, when the active ingredient level was increased to form a more economical concentrate, the concentrate gelled to form a solid, apparently due at least in part to an interaction or attraction between the ethylene-vinyl acetate copolymer, and the nitrogen compound.

Example I, Part B

1
2 Various auxiliary additives mixed into the concen-
3 trates (by mixing for one hour at 120 - 130°F) were found
4 to be effective in lowering the pour point of the concen-
5 trates by improving the compatibility, e.g. inhibiting the
6 interaction of the ethylene-unsaturated ester copolymer and
7 the nitrogen compound. The effect of adding these aux-
8 iliary materials to said concentrates are shown in Table
9 II, which follows.

TABLE II
EFFECT OF COMPATIBILITY IMPROVERS

		Concentrate		Pour Point, °F
		Wt. % A.I.	Wt. % HAN	
1		49.7	49.7	65
2		49.5	49.5	45
3		49.0	49.0	40
4		47.0	49.0	40
5	0.5 Benzoic Acid			
6	1.0 Benzoic Acid			
7	2.0 Benzoic Acid			
8	4.0 Benzoic Acid			
9	0.5 Isobutyric Acid	49.7	49.7	75
10	4.0 Isobutyric Acid	47.0	49.0	40
11	0.5 Oleic Acid	49.7	49.7	85
12	4.0 Oleic Acid	47.0	49	45
13	0.5 Phenol	49.7	49.7	85
14	1.0 Phenol	49.5	49.5	75
15	2.0 Phenol	49	49	70
16	4.0 Phenol	47	49	40

	Wt.% Additive	TABLE II (Cont'd.)	Concentrate		Pour Point, °F
			Wt.% A.I.	Wt.% HAN	
1					
2					
3	0.5 P-Methoxy Phenol		49.7	49.7	85
4	4.0 P-Methoxy Phenol		47	49	50
5	0.5 Maleic Anhydride		49.7	49.7	45
6	4.0 Maleic Anhydride		47.0	49	2 phases
7	0.5 C ₈ Alkyl Succ. Anhydride		49.7	49.7	65
8	4.0 C ₈ Alkyl Succ. Anhydride		47.0	49	40
9	0.5 Tetraisobutyl Succ. Anhydride		49.7	49.7	80
10	4.0 Tetraisobutyl Succ. Anhydride		47.0	49	40
11	0.5 Tetrapropyl Succ. Anhydride		49.7	49.7	65
12	4.0 Tetrapropyl Succ. Anhydride		47.0	49	40
13	0.5 Polyisobutenyl (900 mw) Succ. Anhydride		49.7	49.7	90
14					
15	4.0 Polyisobutenyl (900 mw) Succ. Anhydride		47.0	49	65
16					
17	0.5 Tridecyl Mono Acid Phosphate		49.7	49.7	70
18	4.0 Tridecyl Mono Acid Phosphate		47.0	49	45

1 Looking at Table II, when 0.5 wt. % benzoic
2 acid was mixed with 99.5 wt. % of the concentrate (which
3 was 49.75 wt. % of HAN and 49.75 wt. % of a 50/50 weight
4 mixture of Nitrogen Compound A and Polymer 1) the pour
5 point was 65°F. Table I shows that this represented an
6 improvement since Concentrates A and B were solid at room
7 temperature (about 70°F) and had pour points of 85-90°F.
8 Increasing the benzoic acid to 4.0 wt. % gave a 40°F pour
9 point.

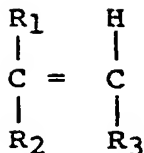
10 Maleic anhydride was very effective at 0.5 wt.
11 %, although the higher concentration of 4.0 wt. % caused
12 the concentrate to separate into two phases as noted. The
13 various succinic anhydrides were effective, although as the
14 hydrocarbon portion increased from the C₈ alkyl group to
15 the 900 molecular weight polyisobutylene group, the
16 effectiveness decreased.

17 In summary, the use of a mild or weak organic
18 acid appears to inhibit the viscosity increasing inter-
19 action of the polar nitrogen compound with the ethy-
20 lene-ester copolymer. This enables the preparation of con-
21 centrates with a higher proportion of active ingredient
22 present while still having good handling properties, e.g.
23 easy to pour or to empty out of the drum or container.

CLAIMS:

1. An additive concentrate for incorporation into wax-containing petroleum fuel oil compositions to improve low temperature flow properties, comprising an oil solution containing about 20 to 70 wt. % diluent oil, and 30 to 80 wt. % of an additive combination of:

- (A) one part by weight of a C_{30} - C_{300} oil-soluble diamide formed by reaction of about two molar proportions of alkyl amine having C_8 to C_{30} alkyl groups with one molar proportion of a C_4 to C_{10} aliphatic acyclic dicarboxylic acid;
- (B) in the range of about 0.005 to 1.0 parts by weight of an oil-soluble organic acid of 6 to 30 carbon atoms, and one to three acid groups, selected from the group consisting of non-linear carboxylic acid, their anhydrides, phenols, and organic acids of phosphorus; and
- (C) in the range of about 0.01 to 10 parts by weight of an oil-soluble ethylene backbone distillate flow-improving polymer having a number average molecular weight in the range of about 500 to 50,000 which is a copolymer consisting essentially of 3 to 40 molar proportions of ethylene per molar proportion of unsaturated ester of the general formula:



wherein R_1 is methyl or hydrogen, R_2 is $-\text{OOCR}_4$ or $-\text{COOR}_4$ where R_4 is a C_1 to C_{28} alkyl group and R_3 is hydrogen or $-\text{COOR}_4$; and wherein said organic acid lowers the viscosity of said oil containing (A) and (C).

2. An additive concentrate according to claim 1, wherein the amount of (B) is in the range of about 0.01 to 0.4 parts, and the amount of (C) is about 0.03 to 5 parts.

3. An additive concentrate according to claims 1 or 2 in which the ethylene copolymer is an ethylene-vinyl acetate copolymer which contains from 4 to 20 molar portions of ethylene per molar portion of vinyl acetate, and has a number average molecular weight from 1,000 to 20,000.

4. An additive concentrate according to claims 1-3 in which the diamide is obtained by the reaction of maleic anhydride with secondary di(hydrogenated tallow) amine.

5. An additive concentrate according to claims 1-4 in which the organic acid (B) is a carboxylic acid.

6. An additive concentrate according to claim 5, in which the organic acid is an aromatic carboxylic acid, fatty acid or an alkyl or alkenyl succinic anhydride.

7. A distillate fuel oil containing said additive concentrate of claims 1-6 in such proportion as to give about 0.001 to 0.5 wt % total of said (A), (B) and (C) components.

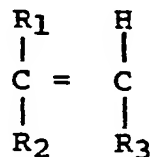
8. A distillate fuel according to claim 7 wherein: (A) is the diamide of maleic anhydride and secondary hydrogenated tallow amine and (C) is a copolymer of 3 to 20 molar proportions of ethylene per molar proportion of vinyl acetate having a number average molecular weight of 1000 to 6000.

9. An additive concentrate for incorporation into wax-containing petroleum fuel oil compositions to improve low temperature flow properties, comprising an oil solution containing about 20 to 70 weight % diluent oil, and about 30 to 80 weight % of an additive combination of:

- (A) about one part by weight of a diamide of maleic anhydride and secondary hydrogenated tallow amine obtained by the reaction of about 2 molar proportions of said amine per molar proportion of said maleic anhydride;
- (B) 0.01 to 0.4 parts of benzoic acid; and
- (C) about 0.03 to 5 parts of an ethylene vinyl acetate copolymer of 4 to 20 molar proportions of ethylene per molar proportion of vinyl acetate, such copolymer having a number average molecular weight of about 1,000 to 6,000; and wherein said benzoic acid lowers the viscosity of said diluent oil containing (A) and (C).

10 The use to improve the flow and filterability properties of distillate fuels at low temperature of an additive concentrate, comprising an oil solution containing about 20 to 70 wt.% diluent oil, and 30 to 80 wt.% of an additive combination of:

- (A) one part by weight of a C_{30} - C_{300} oil-soluble diamide formed by reaction of about two molar proportions of alkyl amine having C_8 to C_{30} alkyl groups with one molar proportion of a C_4 to C_{10} aliphatic acyclic dicarboxylic acid;
- (B) in the range of about 0.005 to 1.0 parts by weight of an oil-soluble organic acid of 6 to 30 carbon atoms, and one to three acid groups, selected from the group consisting of non-linear carboxylic acid, their anhydrides, phenols, and organic acids of phosphorus; and
- (C) in the range of about 0.01 to 10 parts by weight of an oil-soluble ethylene backbone distillate flow-improving polymer having a number average molecular weight in the range of about 500 to 50,000 which is a copolymer consisting essentially of 3 to 40 molar proportions of ethylene per molar proportion of unsaturated ester of the general formula:



wherein R_1 is methyl or hydrogen, R_2 is $-OOCR_4$ or $-COOR_4$ where R_4 is a C_1 to C_{28} alkyl group and R_3 is hydrogen or $-COOR_4$; and wherein said organic acid lowers the viscosity of said oil containing (A) and (C).

(19)



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(54) Additive concentrates for distillate fuels.

(57) An additive concentrate for incorporation into wax containing petroleum fuel oil compositions to improve low temperature flow properties comprising an oil solution containing:

(A) a C₃₀-C₃₀₀ oil-soluble nitrogen salt and/or amide compound wax crystal growth inhibitor formed by reaction of alicyclic C₄ to C₁₀ carboxylic acid and long chain secondary amine;

(B) an organic acid to improve the solubility of (A) in the oil, which acid includes non-linear carboxylic acids including branched or unsaturated fatty acids, aromatic acids, e.g. benzoic acid, phenols, and organic phosphorus containing acids; and

(C) a copolymer of ethylene and an unsaturated ester, e.g. vinyl acetate.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	FR-A-2 300 792 (EXXON) * Claims; page 2, line 37 - page 3, line 31; page 7, line 17 - page 8, line 18; page 10, line 38 - page 11, line 1; table 1,D *	1,3-6, 8-10	C 10 L 1/14 C 10 L 1/18 C 10 L 1/22
A	---	2,7	
P,Y	EP-A-0 104 015 (EXXON) * Claims; abstract; page 5, line 21 - page 10, line 13 *	1,3-6, 8-10	
A	---	2,7	
X	FR-A-2 531 448 (LUBRIZOL) * Claims 1,5-7,11,12,18 *	1,3,10	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	FR-A-2 426 730 (EXXON) * Claims; example 7; page 1, lines 1-7; page 3, line 21 - page 19, line 39 *	1-10	C 10 L
A	US-A-3 850 587 (FROST Jr.) * Abstract; claims; column 3, line 40 - column 5, line 66 *	1,3,5, 6,9,10	

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17-02-1986	Examiner DE LA MORINERIE B.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone. Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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DOCUMENTS CONSIDERED TO BE RELEVANT				Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)	
A	GB-A-1 010 714 (SHELL) * Whole document *	1,10		
A	--- US-A-3 795 495 (HOWLAND et al.) * Abstract; figures; claims *	1,10		
A	--- GB-A-1 473 155 (UNION OIL COMPANY OF CALIFORNIA) * Claims *	1,10		
A	--- US-A-3 558 470 (GILLESPIE et al.) * Abstract; examples; claims *	1,10		
A	--- US-A-4 388 470 (FIELDS et al.) * Whole document *	1,5,6, 10		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)	
The present search report has been drawn up for all claims				
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